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II. IONIZING POTENTIALS OF METHANE, ETHANE, ETHYLENE AND ACETYLENE.

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JOSEPH C. MORRIS, JR.

THESIS

PRESENTED TO THE FACULTY OF PRINCETON UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

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COMPARISON OF MEASUREMENTS OF CRITICAL POTENTIALS OF MERCURY VAPOR

By J. C. Morris, Jr.

Abstract

The critical potentials of Hg vapor were examined with a tube constructed to permit use of a number of different methods. For detecting critical potentials other than those of ionization, the *Hertz method* proved much the most satisfactory. Of the 13 critical potentials found below ionization, 10 have definite spectroscopic interpretation and the remaining 3, which are probably due to mercury molecules, confirm similar values reported by Miss Messenger. The *partial current method* of Franck and Hertz showed less resolving power, but otherwise gave good agreement with the Hertz method. The *Franck and Einsporn method* gave peculiar results, suggesting that it detected only photoelectric effects and not metastable atoms, and that the failure to show the other critical potentials was due to features of tube design which eliminated inelastic impacts in the region around the filament where space charge acts to limit emission.

Compton's method for studying ionization proved very satisfactory since no effects of other types of inelastic impacts were detected. Three *ultra-ionizing potentials* at 10.65, 11.34, 11.78 were found in good agreement with Lawrence, although the present results do not show the regions of maximum ionization probability near these values, as reported by him. An attempt to test the molecular origin of these high ionizing potentials led to negative results.

Introduction

IN THE study of the various energy states to which a neutral atom or molecule may be raised by supplying energy by an electron impact, a number of basically different methods have been developed for the detection, measurement, and classification of these energy levels. Results with various gases and vapors have indicated that the most suitable method varies with the gas or vapor employed. The apparatus described in this paper was designed to be used according to a number of the previously employed methods, and by simple changes in the connections the method could be changed. A comparison of the results obtained using the different methods should show that the observed values of critical potentials are compatible and should indicate which is the most suitable for measuring critical potentials of any particular type.

Measurement of the radiating potentials can be made according to the partial current method of inelastic impacts as employed by Franck and Hertz,[1] the modified Lenard method as employed by Franck and Einsporn,[2] and the Hertz,[3] method for inelastic impacts. Ionizing and non-ionizing potentials can be distinguished in the manner employed by Davis and

[1] Franck and Hertz, Phys. Zeits. **17**, p. 409 (1916).
[2] Franck and Einsporn, Zeits. f. Physik **2**, p. 18 (1920).
[3] Hertz, Zeits. f. Physik **18**, p. 307 (1923).

Goucher[4] or by a modification of the method employed by Compton.[5] Ionization and ultra-ionization potentials can be measured by the detection of positive ions in a chamber similar to that employed by Mackay.[6] This report deals with the results obtained with mercury vapor.

Apparatus

The construction of the tube is shown in Figure 1. Electrons from the filament F are accelerated to H by a variable, measured, electromotive force. Some of these electrons passing through the gauze G_1 enter the field free space S where a number of them will collide with the atoms or molecules present. The sides of the cylindrical electrode H about S are made of gauze as are the coaxial grids G_2 and G_3. The plate P is cylindrical, coaxial with the grids

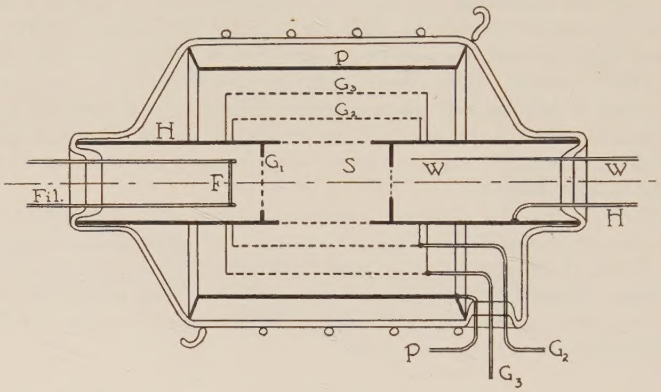

Fig. 1. Construction of the tube.

and mounted at some distance from the sides of the containing glass vessel. In the final form of the tube all metal parts mentioned thus far except the filament are of nickel. In an early experimental tube an aluminum plate was used. Filaments of molybdenum and of tungsten were used at first but later a Wehnelt cathode was employed with greatly improved results. The electrode W is a thin platinum wire mounted in H as shown and removed as far as possible from any direct radiation from S. The purpose of the coil of a few turns of heavy wire wound around the tube will be explained later. The usual precautions of "baking-out" and degassing the metal parts were observed.

The accelerating potential was varied uninterruptedly by steps (0.02 to 0.1 volt) and measured by a voltmeter checked against a potentiometer. In all cases the electron emission from the filament was measured and the observed effect divided by the emission thereby giving readings proportional to the effect of a constant electron stream. The effects produced by the electron bombardment—photoelectric, production of positive ions, etc.—were measured electrically by high sensitivity electrometers or galvanometers.

[4] Davis and Goucher, Phys. Rev. **10**, p. 101 (1917).
[5] Compton, Phil. Mag. **40**, p. 553 (1920).
[6] Mackay, Phil. Mag. **46**, p. 828 (1923).

With most of the readings a null method was employed whereby the electrometer or galvanometer was returned to zero by a counter electromotive force applied by a Leeds and Northrup potentiometer. The readings of the potentiometer are in these cases proportional to the currents being measured. In all cases where scale readings were employed the instrument was calibrated.

Franck and Hertz Method

With the tube connected as shown in Figure 2 it may be used to measure critical potentials by the partial current method of inelastic impact as in the work of Franck and Hertz.[1] The accelerating potential was varied in steps of 0.1 volt while the retarding potential was kept fixed at a value of 0.5 volt which was found to be best after trying values from 0.1 to 1 volt.

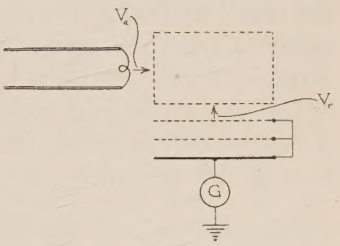

Fig. 2. Connections to give critical potentials by the method of Franck and Hertz.

Mercury vapor was used at pressures corresponding to temperatures from 150°C to room temperature, best results being obtained at the latter temperature. Figure 3 shows the curve obtained and the expected values of critical potentials. The method of determining the correction to be applied to the accelerating potential was as follows. A search was made in the neighborhood of 5 volts for indications of two critical potentials differing from each other by 0.2 volt corresponding to the known critical potentials at 4.7 and 4.9 volts. These were found and the accelerating potential scale was shifted to bring these peaks to the correct value, requiring a shift of about 0.6 volt. The success in accounting for the observed peaks when so corrected justifies the method.

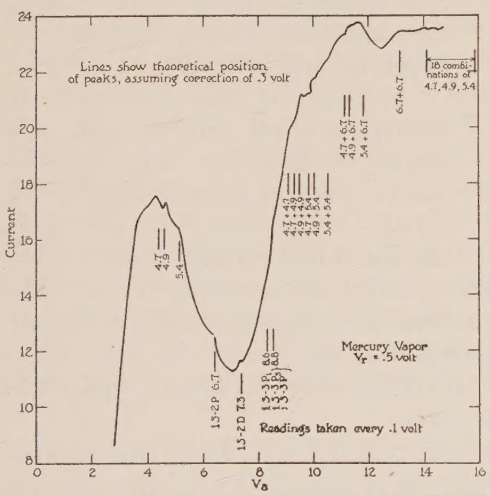
Lines show theoretical position of peaks, assuming correction of .3 volt
16 combinations of 4.7, 4.9, 5.4
Mercury Vapor
V_r = .5 volt
Readings taken every .1 volt
Current
V_a

Fig. 3. Critical potentials of Hg vapor by the method of Franck and Hertz.

While the peaks and bulges observed are in general accounted for it is obvious that this method is hardly suited to serve for accurately locating the critical potentials, especially above eight volts, where the effects of superposition render any separation impossible.

Franck and Einsporn Method

Using similar connections but employing a retarding potential of twenty volts or more the tube was prepared to detect critical potentials according to the method of Franck and Einsporn.[2]

The impact of electrons with atoms in S may: (1) Produce positive ions by ionization of the atom; (2) Excite the atom, *i.e.*, leave the atom in a state of abnormally large energy. Some of these states may be metastable and persist for a finite time; others will be such that the atom spontaneously returns to its normal state with the emission of radiation of frequency ν given by the equation $eV = h\nu$.

The production of radiation, metastable atoms, or positive ions in the space S may be detected with this apparatus. The metastable atoms will in part drift by diffusion and reach the plate where at least a certain proportion will by a mechanism not clearly understood cause the ejection of an electron. Radiation will if of sufficiently high frequency cause photo-electric emission from the plate. Positive ions having diffused through the gauze sides of S will be drawn to P by the applied field V_R. Any one of these effects will produce an electron current from the plate, but will give no clue to the particular cause. As described later the minimum ionizing potential may be determined by independent means, leaving the effects produced by electrons having less than ionizing energy to be explained as being due to either metastable atoms or radiation. Messenger[7] has devised a method for separating these two effects.

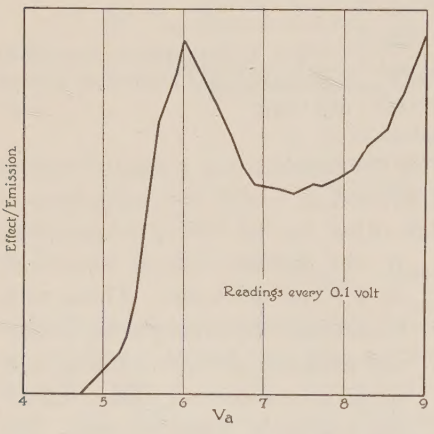

Fig. 4. Critical potentials of Hg vapor by the method of Franck and Einsporn.

The curves obtained were all rather erratic, but all of the general type shown in Figure 4, not showing the numerous breaks expected between 4.7 and 10.4 volts.

Although it was impossible to reproduce these curves with any degree of exactness even for successive runs, the general shape of the curves was preserved, the peak always being present more or less strongly, but at no time was it possible to detect any structure to the curve even when a Wehnelt cathode burned at very low temperatures was employed. The height of the peak varied very much from run to run—at times being five times as high as the subsequent part of the curve, at other times it was represented by only a flattening of the curve.

The function of the coil about the tube is as follows. When connected to a source of high frequency current such as is employed with an induction furnace, it heats the Plate P to a red heat. Such treatment seems to increase the photoelectric sensitivity of the plate, probably by a purely cleaning action. This treatment did not affect the shape of the curves subsequently obtained except perhaps to accentuate the peak a trifle.

[7] Helen A. Messenger, Phys. Rev. **28,** p. 962 (1926).

Changes of pressure of the mercury vapor from that corresponding to 150°C to room temperature did not affect the shape of the curves, but conditions were more steady at room temperature.

A comparison of the general shape of these curves and those of the intensity of the 2537 line plotted against the energy of the exciting electron, as given by White[8] and Crozier,[9] shows a striking similarity, sufficient to warrant the hypothesis that the curves here obtained indicate only the photoelectric effects with little or no contribution due to metastable atoms. If one regards the curves here obtained in this light, they may be thought of as representing jointly the effects of the 2537 line as indicated in the work of White[8] and Crozier[9] and that of the 1849 which, while coming in at 6.7 volts, is not intense until about 7.5 or 8 volts. This last fact was shown by the work of Messenger[7] by removing the effects of metastable atoms from the observations. This was done by shielding the plate with quartz filters which, while transparent to radiation, prevented the diffusion of metastable atoms to the plate.

Why the effect of metastable atoms should have been absent in the present experiments is not clear. The only significant difference in design of the tube used and those tubes in which the effects of metastable atoms have been observed is that the detecting plate is here parallel to the direction of the bombarding stream of electrons while in the other cases the plate was perpendicular to the electron stream. However, there seems to be no reason why the uncharged, metastable atoms should have any greater tendency to diffuse in one direction rather than in another.

Considering the possibility that the present unexpected results were due to the fact that the apparatus was unusually sensitive to photoelectric action and that the effect of the metastable atoms was being relatively masked, it was decided to make a run when the photoelectric sensitivity was unusually low. By avoiding the conditions for optimum photoelectric sensitivity (especially clean, degassed surfaces, etc.) the effect on the detecting system was reduced to 1/60 of its previous value, but a run made under these conditions showed no difference from other runs. However, this negative result is not very significant for with no definite knowledge of the mechanism whereby metastable atoms cause the ejection of electrons from a plate with which they come in contact, it is quite possible that this phenomenon may be in part photoelectric and that any reduction of the photoelectric sensitivity of the detecting plate would reduce the effects due to radiation or metastable atoms by the same factor.

Various detecting systems consisting of plate, one or two of the grids, and plate and grids together were tried all giving the same results. This precludes the possibility that the metastable atoms had been filtered out by the grids.

[8] D. R. White, Phys. Rev. **28**, p. 1123 (1926).

[9] Wm. D. Crozier, Paper No. 20 Presented at the meeting of the American Physical Society, Chicago, Ill., November, 1927. The writer is indebted to Mr. Crozier for a copy of his results.

In discussing these results Professor Franck has pointed out that in the original experiments by Franck and Einsporn it was possible to note the critical potentials as breaks in a curve showing the primary electron emission plotted against accelerating potentials. This was also observed in the work of Messenger but was not observed in the present experiments, although looked for. The explanation of this difference probably lies in the fact that the filament was so close to the accelerating gauze that at the pressure of mercury vapor employed the probability of a collision between an electron and mercury atom in this space was very low, so that there was no variation in the limiting effect of space charge due to inelastic impacts of electrons in this region.

The correction to be applied to the accelerating potential scale was determined by measuring the minimum ionizing potential (the value of which is known from spectroscopic data to be 10.4 volts) by the method to be described later and applying the correction to the accelerating potential scale required to bring the observed value to 10.4 volts. The correction necessary was of the order of 0.6 volt and checked the corrections made in the manner described under the Franck and Hertz method.

Hertz Method

Using again a small retarding potential of 0.1 volt and arranging switches so that this could be made 0 or 0.1 volt at will, and plotting the difference of the galvanometer readings for these two cases as ordinate against the accelerating potential as abscissa, the tube was used according to the Hertz[3]

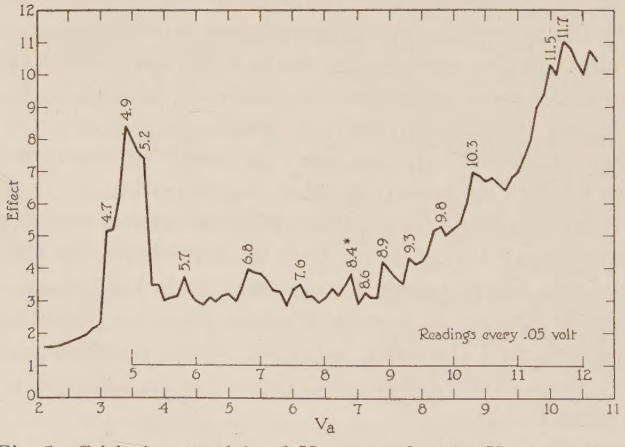

Fig. 5. Critical potentials of Hg vapor by the Hertz method.

method for determining the critical potentials of inelastic impacts. This was by far the most efficient method of all used for determining critical potentials below ionization. Figure 5 shows a set of the results obtained with this method and gives the values of the more prominent potentials noted. The accompanying table shows the interpretation placed on the various potentials. The curves obtained with this method could be reproduced without difficulty.

The curves were taken at various temperatures from 100°C to room temperature, best results being obtained at the latter temperature. The correction to be applied to the accelerating potential scale was determined in the manner described under the Franck and Hertz method.

Distinguishing Ionizing from Non-Ionizing Potentials

For the purpose of distinguishing radiating from ionizing potentials either the Davis and Goucher method or a modification of the Compton may be used. The latter method as employed in these experiments consists in using as collector alternately the large photoelectrically sensitive plate P and the small platinum wire W (shielded from radiation from S) as the collecting electrode. In the first case the ratio of the intensity of the effects produced by radiation to those produced by ionization would be relatively high compared to the same ratio when using the wire collector. In fact with Hg vapor no effect was obtained using the small wire collector below 10.4 volts showing that no critical potentials below that value could be termed ionizing potentials.

Table I. *Results obtained using Hertz method.*

Pot. observed (volts)	Interpreted from Theory	Calculated from Theory	Remarks
4.7	$1^1S-2^3P_0$	4.66	Metastable state
4.9	$1^1S-2^3P_1$	4.86	2537
5.2			5.25 obs. by Messenger
5.4	$1^1S-2^3P_2$	5.43	Metastable state
5.7	2^3P_0	5.73	Ionization of metastable excited atom
6.8	1^1S-2^1P	6.67	
7.6	1^1S-2^3S	7.69	
8.1			8.0 and 8.05 obs. by Messenger
8.4			8.35 obs. by F. & E. 8.3 obs. by Messenger
8.6	$1^1S-3^3P_{0,1}$	8.58	
8.9	1^1S-3^1P	8.79	
	$1^1S-3^3D_{1,2,3}$	8.82	
	1^1S-3D	8.80	
	$1^1S-3^3P_2$	8.80	
9.3	$2(1^1S-2^3P_0)$	9.32	Successive impact
9.8	$2(1^1S-2^3P_1)$	9.8	Successive impact
10.3	1^1S	10.39	Ionization
	6.7+4.9		
11.5	6.7+4.7		

As both these methods are purely qualitative no curves are here given.

Ionizing Potentials

The minimum ionizing potential can be roughly determined by observing the upward break in the plate current-plate potential curve, caused by the partial neutralization of space charge by positive ions. This method is suitable for only the roughest of determinations even when the curves are plotted in the manner suggested by Langmuir,[10] and employed by Found[11]

[10] Langmuir, Phys. Rev. **2**, p. 457 (1913).

[11] Found, Phys. Rev. **16**, p. 41 (1920).

Using this method the ionizing potential of mercury could be shown to be in the neighborhood of 10.5 volts.

The most interesting phase of this experiment was the determination of the ionizing and ultra-ionizing potentials of mercury vapor by the more accurate method suggested in the preceding section.

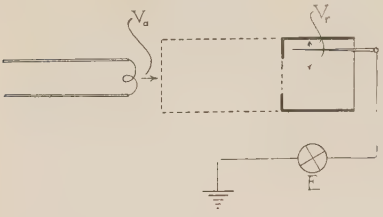

Fig. 6. Connections for obtaining the ionizing and ultra-ionizing potentials in Hg vapor.

Figure 6 shows the connections employed. It is to be noted that an electron current from the wire *W* might be due to photoelectric emission from the wire due to radiation, metastable atoms diffusing to the wire, or positive ions drawn to the wire by the applied retarding field. But as the wire is of platinum, is of small area, and is shielded from direct radiation the first two of the causes indicated above will have little or no opportunity to contribute to the electron current from the wire. This is born out by experiment, and the curves obtained represent ionization currents only.

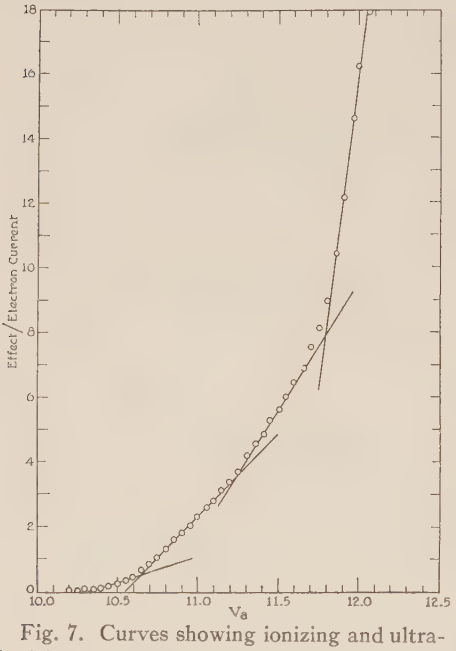

Fig. 7. Curves showing ionizing and ultra-ionizing potentials in Hg vapor.

When first tried using a molybdenum filament, the curve obtained was fairly smooth and showed only an uncertain suggestion of breaks above the minimum ionizing potential as had been reported by Lawrence.[12] In a further effort to locate these breaks a Wehnelt filament so nicked as to be an almost equipotential source was employed and burned at such a temperature that only the slightest redness was observable. Taking these precautions to reduce the velocity distributions of the bombarding electron stream, the curve shown in Figure 7 was obtained showing critical potentials above the minimum ionizing potential. The values of these critical potentials check closely those obtained by Lawrence. Unlike the curves obtained by him the probability of ionization appears from these curves to be proportional to the excess of energy of the electron over the amount required to produce this state. The constant of proportionality is measured by the slope of the curve. The relative value of the constant of proportionality after each break is as follows:

[12] Lawrence, Phys. Rev. **28**, p. 945 (1926); Lawrence, Jour. of the Franklin Institute. p. 91 (July 1927).

Critical Potential	10.4	10.65	11.34	11.78
Constant of Proportionality	0.36	1.03	1.54	8.00

The constant of proportionality for each type of ionization as measured by the difference of slope before and after each break are to each other as follows:

Critical Potential	10.4	10.65	11.34	11.78
Constant of Proportionality	.36	.67	.51	6.5

The curves showing this linear relationship between excess electron energy and number of positive ions formed extend over a range of only a few volts and hence this conclusion is in no wise at variance with the fact that the probability of ionization reaches a maximum at about 125 volts as shown in the work of Compton and Van Voorhis.[13]

Considering the possibility that these ultra ionizing potentials were of a molecular origin, the experiment was tried in superheated vapor at higher temperatures. Since the energy of dissociation of a mercury molecule is but slightly larger than the mean kinetic energy of a molecule at room temperature, a slight increase in temperature should greatly decrease the relative concentration of molecules to atoms, and curves taken at elevated temperatures should show critical potentials of molceular origin less prominently. No such effect was noted in the case of these ultra ionizing potentials.

The results obtained employing the various methods as has been described, are all compatible with each other and the results given for each method indicate its value for determining the critical potential of any type.

The writer wishes to acknowledge his indebtedness to the members of the Physics Department, especially to Professor K. T. Compton who suggested the problem and under whose guidance the work was carried out. He is also indebted to Professor Webb and Miss Messenger of Columbia University, for opportunity to discuss with them some of the problems which have arisen during the course of the work.

Palmer Physical Laboratory,
Princeton, N. J.
June 2, 1928.

[13] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26**, p. 436 (1925).

IONIZING POTENTIALS OF METHANE, ETHANE, ETHYLENE, AND ACETYLENE

By J. C. Morris, Jr.

Abstract

After preparation and purification by the most approved methods, the gases *methane, ethane, ethylene* and *acetylene* were introduced into an ionization tube of the Mackay type and their ionization potentials measured. The calibration of the apparatus was made with the aid of Hg vapor and He gas as standards. The values found are: methane 14.4 volts, ethane 12.8 volts, ethylene 12.2 volts, acetylene 12.3 volts, and are believed to be correct within 0.2 volt.

THE method devised by Mackay[1] to measure ionizing potentials, having been found satisfactory for use with polyatomic gases, was employed with methane, ethane, acetylene, and ethylene.

The tube used was similar in all respects to the one used by Mackay except that it was slightly larger, giving a larger electron emission and hence larger positive ion currents. For description of the apparatus and method of taking measurements the reader is referred to the papers of Mackay mentioned above. Mercury vapor and helium were used as standards for calibration purposes, the ionizing potential of mercury being taken to be 10.4 volts and that of helium as 24.5 volt.

The gases employed were prepared as follows:

Methane: Methane was prepared by heating a mixture of sodium acetate and soda lime. The gas evolved was passed through concentrated caustic potash solution and then through concentrated sulfuric acid. The gas was then liquefied and allowed to evaporate, the middle third being kept for the purposes of the experiment.

Ethane: The gas was prepared by the action of the zinc-copper couple on ethyl iodide. The gas evolved was passed through alcohol and then through concentrated sulfuric acid. The gas was then liquefied with liquid air and allowed to evaporate, the middle third being kept for the purposes of the experiment.

Ethylene: The gas was generated by the reaction of ethyl alcohol with concentrated sulfuric acid. The gas evolved was passed through concentrated caustic soda solution to remove CO_2 and SO_2 and then through concentrated sulfuric acid. The gas was then liquefied with liquid air and allowed to evaporate, the middle third being kept for the purposes of the experiment.

A tank of the best commercial ethylene being available, some of this gas was purified in the manner described above and used in some of the measurements. No difference could be detected in the ionizing potential of this gas and the gas prepared.

[1] Mackay, Phil. Mag. **46,** p. 828 (1923); Phys. Rev. **24,** p. 319 (1924).

Acetylene: Acetylene from a commercial tank was purified by passing through water, silver nitrate solution, caustic soda solution, and concentrated sulfuric acid. The gas was then solidified and allowed to sublime the middle third being kept for the purposes of the experiment.

A number of measurements were taken with each gas and the values obtained averaged after correcting for initial velocity and contact difference of potentials by comparison with helium and mercury vapor as standards.

The values obtained are given in Table I.

TABLE I. *Ionization potentials of methane, ethane, ethylene and acetylene.*

Gas	Ioniz. Pot. observed (volts)	Previously reported values (volts)	Observer
Methane	14.4	9.5	Hughes & Dixon[2]*
		13.5	Mayer[3]*
		12.5	Pietsch[4]
		13.9	Hughes & Klein[5]
		14.4–15.2	Glockler[6]
		14.58	Pietsch & Wilcke[7]
Ethane	12.8	10.	Hughes & Dixon[2]*
Ethylene	12.2	9.85	" " "
Acetylene	12.3	9.95	" " "

* These investigations were made prior to knowledge of the distinction between ionizing and radiating critical potentials.

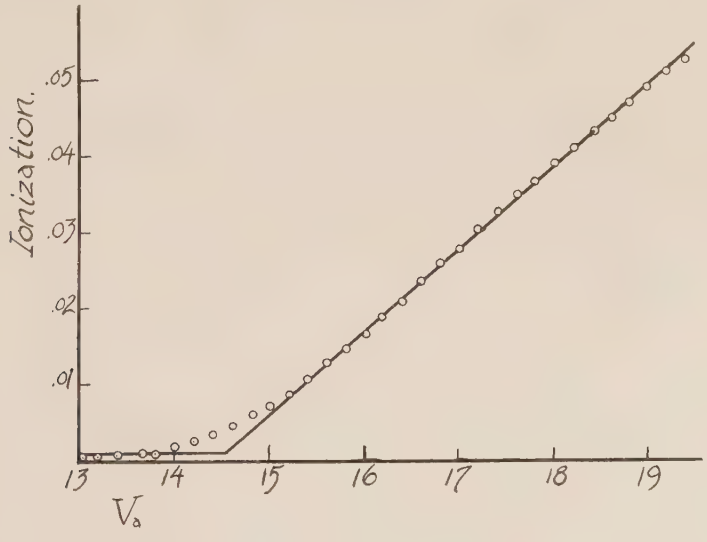

Fig. 1. Ionization curve for methane.

The curves shown are typical examples of the curves obtained with this method. The method employed has the disadvantage that there is a con-

[2] Hughes and Dixon, Phys. Rev., **10,** p. 495, 1917.
[3] F. Mayer, Ann. d. Phys. (4) **45,** p. 1, 1914.
[4] E. Pietsch, Dissert. Berlin 1926, S34.
[5] Hughes and Klein, Phys. Rev., **23,** p. 450, 1924.
[6] Glockler, Journ. Amer. Chem. Soc., **48,** p. 2021, 1926.
[7] Pietsch and Wilcke, Zeits. f. Phys. **43,** p. 342, 1927

siderable velocity distribution among the electrons of the bombarding stream and some critical potentials may not have been detected. It is believed that these values are the principal ionizing potential to within 0.2 volt.

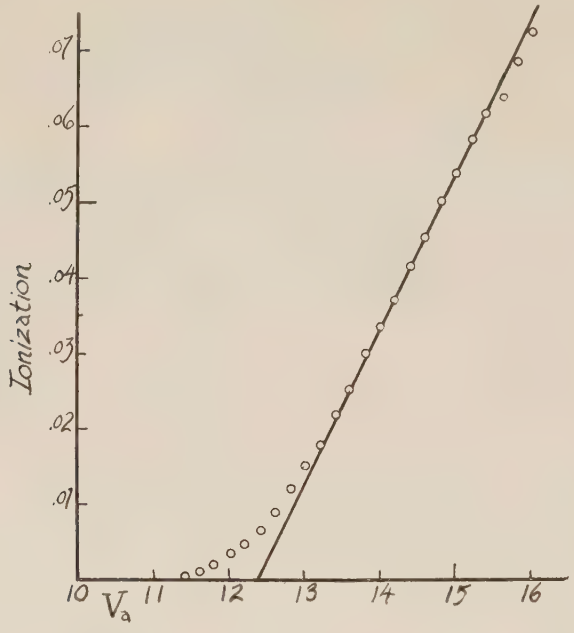

Fig. 2. Ionization curve for acetylene.

The writer wishes to express his appreciation to Dr. C. A. Mackay under whom this work was begun and to Professor K. T. Compton for assistance during the course of these measurements.

Palmer Physical Laboratory,
Princeton, N. J.
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